

# PATENT SPECIFICATION

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(54) A PROCESS FOR THE CONVERSION OF  
HALOPHTHALIMIDOQUINOPHTHALONES  
INTO PIGMENTARY FORM

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The invention relates to a process for the conversion of halophthalimidoquinophthalones into a pigmentary form.

New yellow dyes of the phthalimidoquinophthalone series which have extremely good thermal stability and excellent fastness to light and weather are disclosed in British Patent Specification 1,225,336. Because of their extremely sparing solubility in organic solvents and water these dyes have excellent fastness to solvents and migration and for this reason these dyes should be outstanding pigments.

Regarded tinctorially however the dyes have only limited use as pigments because when they are incorporated into surface coating compositions, printing inks or plastics such as polyethylene and flexible or rigid PVC under conditions conventionally used in industry only pale brownish yellow and turbid colorations are obtained.

The tinctorial properties of the dyes moreover cannot be significantly improved by dissolving them in concentrated sulphuric acid and precipitating them. Since the dyes are only soluble in sulphuric acid of more than 90% by weight strength the dissolution and reprecipitation has to be carried out in and from sulphuric acid of from 90 to 100% by weight strength. In the process of dissolving and reprecipitating from sulphuric acid of more than 90% by weight strength chemical degradation and sulphonation may however take place so that there is deterioration in the tinctorial properties such as fastness to solvents and to migration of the product precipitated.

As will be appreciated from the specific Examples which follow, this invention pro-

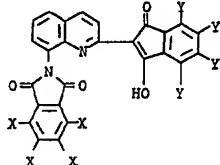
vides a process enabling the production of pigmentary form halophthalimidoquinophthalones which are interesting for pigmentary purposes because of good fastness properties and great colour strength and which have not suffered deleteriously as regards other valuable properties as a result of the conversion of the crude pigment to pigmentary form.

According to the invention, there is provided a process for the conversion into pigmentary form of a chloro- and/or bromo-substituted phthalimidoquinophthalone crude pigment which process comprises grinding the crude pigment optionally in the presence of a grinding aid until the mean size of the primary particles is less than 0.5 micron and contacting the so ground crude pigment with an organic liquid.

In this specification, the expression "mean size of the primary particles" means the numerical mean size of the primary particles.

The process of the invention is generally carried out by grinding the dry dye (hereinafter also termed the crude pigment) which has been obtained as described in British Patent Specification No. 1,225,336 until the mean size of the primary particles is less than 0.5 micron, and preferably 0.1 micron or less. The primary particles in the ground material are agglomerated, the size of the agglomerates in general being on average from 10 to 100 microns. The dry ground material obtained is contacted in a separate step with an organic liquid, advantageously until the pigment exhibits optimum colour strength. The pigmentary product is then separated by a conventional method from the liquid and isolated.

Phthalimidoquinophthalones of the formula:



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in which X is chloro or bromo and Y is chloro or bromo are particularly suitable for the process of the invention.	propanediol, 1,3-propanediol, cyclohexanol, methycyclohexanol, benzyl alcohol and $\beta$ -phenylethanol.	
Grinding may be carried out in the presence or preferably in the absence of grinding aids. Examples of grinding aids are water-soluble salts such as rock salt, sodium sulphate and calcium chloride.	Examples of ketones are: methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, diethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, cyclopentanone, cyclohexanone, methylcyclohexanone, acetophenone and propiophenone.	70
The size reduction may be carried out in planetary ball mills, vibrating mills, ball mills or stirred ball mills and preferably in ball mills having iron balls. Depending on the mill, the grinding aid (if any) and the extent to which the mill is filled, the grinding process generally takes from ten to seventy hours before the material has a mean primary particle size of less than 0.5 micron and preferably not more than 0.1 micron.	Formic acid, acetic acid, propionic acid and butyric acid are particularly suitable as lower aliphatic carboxylic acids.	75
The material thus obtained is a lemon yellow powder which has a bulk density which is from about 20 to 25% higher than that of the crude pigment. In the X-ray spectrum of the ground material the reflexes which are strongly pronounced in the spectrum of the crude pigment are blurred and the widths at half-maximum intensity of the reflux bands are as a rule doubled.	Particularly suitable carboxamides are the N,N-dialkylamides of formic acid, acetic acid and propionic acid such as N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, N,N-diethylacetamide, N,N-dimethylpropionamide, N,N-diethylpropionamide and suitable cyclic carboxamides include N-methylpyrrolidone.	80
In general, dry ground material will be removed from the apparatus used to prepare it and introducing into a volume of the organic liquid. Upon introduction of dry ground crude pigment into the organic liquid, the two phase will in practice be homogenized to achieve efficient particle/liquid contact.	Examples of suitable cyclic aromatic hydrocarbons, aromatic chlorohydrocarbons and nitrohydrocarbons are: toluene, xylene, chlorobenzene, o-dichlorobenzene, trichlorobenzene, nitrobenzene, naphthalene and the methylnaphthalenes. Examples of aliphatic or cyclic ethers are dipropyl ether, diisopropyl ether, dibutyl ether, diisobutyl ether, tetrahydrofuran, dioxane, and diethylene glycol dimethyl or diethyl ether.	85
The properties of the pigment, for example as regards transparency or hiding power or dispersibility, can be influenced by choice of suitable organic liquids, by choice of temperature, at which the liquid/particle contact is carried out and by the duration of the contact without the fastness to light, weather, migration or solvents of the pigmentary product obtained being appreciably affected.	The contact of the ground material with the organic liquid may also be carried out with mixture of two or more of the organic liquids, if desired.	90
Particularly suitable organic liquids are primary, secondary and tertiary aliphatic, cycloaliphatic and arylaliphatic (e.g. phenylaliphatic) alcohols of, for example, up to ten carbon atoms, aliphatic ketones, cycloaliphatic ketones and aliphatic-aromatic ketones of, for example, up to ten carbon atoms, lower aliphatic carboxylic acids of one to four carbon atoms, lower aliphatic carboxamides, cyclic aromatic hydrocarbons, aromatic nitrohydrocarbons and chlorohydrocarbons, and aliphatic and saturated cyclic ethers.	It is preferred to use for the organic liquid/particle contact (which is hereinafter also referred to as conditioning) those of the said organic liquids which can be easily removed during processing, for example by washing out with water, by azeotropic distillation with water, by steam distillation or by drying the entire mixture, for example by freeze drying.	95
Specific example of alcohols are: methanol, ethanol, propanol, isopropanol, butanol, isobutanol, amyl alcohol, isoamyl alcohol, n-hexanol, isohexanol, heptanol, octanol, 2-ethylhexanol-1, tert.-butanol, glycol monomethyl ether, glycol monoethyl ether and glycol monobutyl ether, diethylene glycol monomethyl and monoethyl ether, glycol, 1,2-	The first group includes water-miscible alcohols, ketones, ethers, carboxylic acids and carboxamides such as ethanol, propanol, n-butanol, isobutanol, acetone, dioxane, tetrahydrofuran, formic acid, acetic acid, propionic acid, formamide, N,N-dimethylformamide, ethylene glycol, ethylene glycol monomethyl, monoethyl and monobutyl ether, diethylene glycol diethyl ether and mixtures of these solvents.	100
	Suitable solvents which can easily be removed by azeotropic distillation with water or by steam distillation include the lower alcohols methanol, ethanol, propanol and particularly n-butanol and isobutanol; methyl ethyl ketone, diethyl ketone and the cyclic ethers dioxane and particularly tetrahydrofuran, and aromatic hydrocarbons such as benzene, xylene, chlorobenzene and particularly toluene.	105
	When the entire mixture is to be dried, it is preferred to use liquids which can be	110
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evaporated without leaving a residue and without decomposing, preferably those whose boiling point is below 150°C. Examples of such solvents are alcohols of up to five carbon atoms such as methanol, ethanol, the propanols, the butanols, the pentanols and especially isobutanol, ethanol and propanol, ketones such as methyl ethyl ketone, ethers such as tetrahydrofuran and dioxane, cyclic hydrocarbons such as cyclohexane, benzene, toluene, xylene and chlorobenzene or mixtures of the same.

Contact of the ground material with the organic liquid generally takes place at a temperature of from ambient temperature to 200°C depending on the process for which the pigment is intended or whether a transparent or hiding pigment is desired. To obtain a transparent pigment the contact is preferably carried out at a temperature of from ambient temperature to 80°C. To prepare hiding pigments the contact with the organic liquid is preferably carried out at from 130° to 200°C.

The amount of organic liquid is not generally critical and may therefore be varied within wide limits. The minimum amount of organic liquid is determined in practice by the necessity for the mixture to be mixable before, during and after conditioning and capable of being removed from the apparatus.

The concentration of ground materials is as a rule chosen as high as possible in order to achieve maximum space-time yields in the conversion into the pigmentary form.

The amount of organic liquid is generally from 0.3 to twenty times and preferably from 0.5 to three times the weight of ground material.

Conditioning of the ground material in the organic liquid may be carried out by stirring, kneading, grinding or even by simply leaving the ground material in the organic liquid, depending on the flow behaviour of the mixture.

The duration of the treatment depends especially on the temperature and the particular organic liquid used. The conversion is generally over after from one to fifty hours.

For example, if the ground material (which has been obtained by dry grinding in a ball mill for thirty-six hours the reaction product of tetrachlorophthalic anhydride with 8-aminoquinaldine described in British Patent Specification No. 1,225,336, Example 1) is brought into contact with three times its weight of N,N - dimethylformamide at 140°C a high tinctorial strength, easily dispersible, pure-shade, yellow pigment is obtained. The size of the primary particles is from 0.1 to 0.3 micron. The pigmentary product obtained has about five times the colour strength of the crude pigment and in colouration shows good hiding power in the pure shade. In

spite of the considerably higher colour strength the pigment obtained has a fastness to weather and light which is just as excellent as that of the crude pigment even in pale shades.

When the same ground material is contacted with twice its weight of acetone at 30°C for forty hours there is obtained a very deeply coloured, easily dispersible pigment of pure shade whose primary particle size is from about 0.02 to 0.05 micron. The pigmentary product obtained has about eight times the colour strength of the crude pigment and exhibits in the case of colourations in the pure shade (i.e. in the absence of hiding pigments such as white pigments) high transparency so that the pigment is particularly suitable for the production of printing inks for multi-colour printing. In spite of the considerably higher colour strength, the pigmentary product has a light fastness just as excellent as that of the crude pigment even in pale colourations.

The pigmentary products can be isolated from the treatment mixture by a conventional method, for example by introduction into water and separation of the pigment from the aqueous phase by filtration, centrifuging or decantation.

When liquids which are insoluble in water, or which forms azeotropes with water are used, these may be separated from the pigment by, for example, steam distillation or by dilution of the reaction mixture with a water-miscible solvent, for example methanol or acetone, and filtration. The filter residue is in practice washed with the solvent and water.

Particularly valuable pigments are obtained when, after conditioning, the pigment is isolated from the mixture by freeze drying. For this purpose, the conversion into pigmentary form may be carried out in a suitable organic liquid which solidifies at above -10°C such as p-xylene, dioxane, tert.-butanol, cyclohexane, xylene or acetic acid, and the treatment mixture may be immediately freeze dried. Conditioning may, however, be carried out in another suitable organic liquid and after conversion into the pigmentary form the organic liquid may be separated, the pigment washed with an organic liquid suitable for freeze drying and the pigment then isolated from this liquid by freeze drying. The pigments obtained by freeze drying are particularly easy to disperse so that depending on the treatment temperature, the duration of treatment and the solvent pigments can be obtained which are either hiding or transparent in the pure shade.

The pigments which are obtainable by freeze drying immediately give the total colour strength upon being rolled to 160°C into thermoplastics such as flexible and rigid polyvinyl chloride. There is no increase in

15	colour strength of the rolled sample upon subsequent cold rolling.	65
5	Conversion into the pigmentary form may also be carried out by use as the organic liquid of an organic liquid which contains a resin, binder, plasticizer or other additive such as is conventionally used in the production of surface coatings or printing inks, stoving enamels or formulations for colouring plastics. In these cases, the conversion into the pigmentary form may be combined with the dispersion of the same for the intended purpose.	70
10	Thus, for example, the ground material obtainable by grinding the dye described in Example 1 of British Patent Specification No. 1,225,336 may be converted into the pigmentary form in a stoving enamel which contains an alkyd resin dissolved in a solvent such as butanol, xylene and ethylene glycol monoethyl ether by stirring for from five to ten hours at 120°C so that a ready-made and high-yielding stoving enamel is immediately obtained. Surface coatings obtained therewith exhibit high brilliance, purity and excellent fastness to light, weather and migration. When the crude pigment obtained by the manufacture is used instead of the ground material feebly coloured brownish yellow surface coatings are obtained.	75
15	Conversion into the pigmentary form may be carried out by carrying out grinding of the crude pigment in the presence of the organic liquid. In this embodiment of the invention, the pigmentary product obtained is not always as good as when the previously finely dry ground crude pigment is treated. The pigments thus obtained may after grinding be subjected to a subsequent treatment with an organic liquid to produce a pigmentary form product of more equivalent tinctorial properties to one which has been obtained by dry grinding followed by treatment with the same organic liquid.	80
20	The following Examples will further illustrate the process according to the invention. Parts and percentages hereinafter given are by weight. Parts by volume bear the same relation to parts by weight as the litre to the kilogram.	85
25	<b>EXAMPLE 1</b> (a) 400 parts of the dye prepared according to Example 1 of British Patent Specification No. 1,225,336 are agitated for thirty-six hours in a vibrating mill (4000 parts by volume) filled with 5500 parts of iron balls having a diameter of from 1 to 2.5 cm on an oscillating support. A lemon yellow ground material of increased bulk density is thus formed from the previously brownish yellow powder.	90
30	As is apparent from the X-ray diffraction pattern of a sample the crystal lattice has been substantially destroyed by the grinding and	95
35	this can be recognized by the flattening of the diffraction lines.	105
40	The rise in temperature achievable upon introduction into an organic solvent is another characteristic. When 50 parts of xylene are placed at ambient temperature in a well-insulated vessel, for example a Dewar vessel, and 50 parts of the dye obtained according to Example 1 of British Patent Specification No. 1,225,336 is introduced, a rise in temperature of 0.7°C can be measured after five minutes. When the same quantity of the ground material is introduced, the temperature rises in five minutes by 4.5°C.	110
45	(b) 50 parts of the ground material from (a) and 150 parts of dimethylformamide are stirred for fifteen hours at from 130° to 150°C, then diluted with 800 parts of water and stirred for another three hours at from 70° to 90°C. The pigment is suction filtered, washed well with water and dried at 80°C in a through-circulation cabinet.	120
50	After incorporation into a surface coating or varnish there are obtained deeply coloured greenish yellow surface coatings which as compared with surface coatings which have been prepared with the untreated yellow pigment have five times the colour strength, increased purity and a more greenish tone. The pigment obtained is very easily dispersible. Thus in a stoving varnish upon dispersion in a three roll mill 95% of the achievable final colour strength is achieved after three passes with a pressing pressure of 15 atmospheres gauge and the achievable final colour strength is achieved after six passes at a pressing pressure of 80 atmospheres gauge. Fastness to weather is excellent even in heavily brightened coatings.	125
55	<b>EXAMPLE 2</b> 50 parts of the ground material obtained according to Example 1(a), 63 parts of methyl ethyl ketone and 106 parts of water are boiled under reflux for from five to ten hours. The solvent is then distilled off azeotropically at 70°C. When the boiling point of 100°C has been achieved at the end of the distillation the product is suction filtered, the filtered material is dried at 80° in a through-circulation dryer and finally powdered. A greenish yellow and pure pigment is obtained which is just as deep in colour as that according to Example 1(b). The pigment is however not quite so easily dispersible, in full tone is slightly more transparent and in pale colourations in surface coatings or varnishes is not quite as fast to weather as the pigment obtained according to Example 1(b). Similar pigments are obtained when the methyl ethyl ketone is replaced by tetrahydrofuran or butanol.	130
60	<b>EXAMPLE 3</b> 250 parts of the ground material obtained	135

according to Example 1(a) is introduced into 500 parts of p-xylene and the mixture is stirred for sixteen hours at room temperature. The pigment is then isolated by freeze drying. A very pure, deep-shade greenish yellow pigment is obtained with high transparency which is eminently suitable for the production of printing inks.

A deeply coloured yellowish green intaglio printing ink which has a pure shade may be prepared by simply stirring the pigment with a toluene intaglio printing binder.

#### EXAMPLE 4

The procedure of Example 3 is repeated but the ground material is treated for sixteen hours at 170°C with p-xylene. After freeze drying there is obtained a deep-shade yellow pigment which is pure in shade, which has good hiding power in the pure tone and which moreover may be dispersed very easily not only in surface coatings and varnish but also in thermoplastics, for example flexible or rigid PVC, polyethylene or polypropylene.

#### EXAMPLE 5

8.0 parts of the pigment obtained according to Example 4 is stirred in a solution of 32.2 parts of a rosin-modified phenol resin in 59.8 parts of toluene for thirty minutes with a dissolver ( $n=2000$ ). The pigment suspension is then dispersed by a single pass through a three roll mill at a roll pressure of 60 atmospheres gauge.

A transparent and deeply coloured printing ink is obtained. When the crude pigment is treated in the same way, only a weakly coloured and turbid printing ink is obtained.

#### EXAMPLE 6

(a) 280 parts of the ground material obtained according to Example 1(a) is introduced into 450 parts of p-xylene while stirring. After the air has been expelled the mixture is heated to 136°C and after the apparatus has been closed for ten hours at 160° to 170°C under the autogenous pressure. An internal pressure of 3 bar is thus set up.

The mixture is diluted with methanol and the pigment is suction filtered and washed with methanol and water.

A greenish yellow pigment is obtained which is of great hiding power in the pure shade, extremely fast to weather and which gives colourations of high purity. The pigment may be incorporated very easily into surface coatings, printing inks and plastics such as flexible PVC or polyethylene by rolling at 160°C. Further rolling at ambient temperature does not produce any gain in colour strength.

(b) The same result is obtained when the mixture is solidified by cooling and the pigment is isolated by freeze drying.

When the p-xylene is replaced by the same amount of nitrobenzene and the procedure described under (a) is repeated, a pigment is obtained which in strength, hue and purity as well as in fastness to light and weather has similar properties.

#### EXAMPLE 7

7.5 parts of the ground material obtainable according to Example 1(a) and 44 parts of a baking enamel (consisting of 67 parts of an alkyd resin based on coconut oil, 60% in xylene, 17 parts of a urea-formaldehyde-butanol condensation product, 60% in n-butanol and 16 parts of ethylene glycol monoethyl ether) are stirred at 120°C for ten hours.

A yellowish green paint is obtained which has a pure hue and good hiding power. As compared with a coating prepared from the crude pigment the colour strength is five times as great, and the hue is more greenish and considerably purer.

The following procedure in accordance with DIN 53,234 is followed to determine colour strength: 2 parts of the paint prepared according to Example 7 is mixed with 12 parts of a white coating consisting of 20 parts of titanium dioxide (rutile) and 80 parts of a solution of 67 parts of an alkyd resin based on coconut oil (60% dissolved in xylene) and 17 parts of a urea-formaldehyde-butanol condensation product (60% dissolved in n-butanol) and 16 parts of ethylene glycol monoethyl ether. The coating obtained is applied to sheet metal or cardboard by spraying, or by pouring and knife-coating, and then baked for thirty minutes at 130°C. Tintorial evaluation is carried out according to the FIAF scheme (Farbe + Lack 75, pages 854 to 862 (1969)).

#### EXAMPLE 8

The procedure described in Example 1(b) is repeated but the dimethylformamide is replaced by the same weight of N-methyl-pyrrolidone. The mixture is heated for fifteen hours at 170°C and worked up as described in Example 1(b).

A pigment is obtained which is somewhat weaker in colour but which is particularly pure, hiding and readily dispersible.

#### EXAMPLE 9

400 parts by volume of polyamide plastics beads of a diameter of 1 mm, 200 parts by volume of tert.-butanol and 30 parts of the dye (crude pigment) obtained according to Example 1 of British Patent Specification No. 1,225,336 are ground for 36 hours in a laboratory attrition mill having an effective capacity of 500 parts by volume. An internal temperature of 55°C is thus set up. The mixture is solidified and the pigment is iso-

lated from the beads by freeze drying followed by screening.

A particularly deep-shade, transparent pigment is obtained which is pure in hue and  
5. may be very readily incorporated into printing varnishes.

The mixture may also be isolated as described in Example 1(b). A deep-shade, transparent pigment is then obtained which has a pure hue and which has practically the same properties as that isolated by freeze drying.

#### EXAMPLE 10

150 parts of xylene, 15 parts of crude pigment (prepared according to Example 1 of British Patent Specification No. 1,225,336) and 200 parts by volume of glass spheres (diameter 3 mm) are stirred for fifteen hours at 130° to 136°C. The glass spheres are filtered off and the pigment suspension is  
10 worked up as described in Example 6. An easily dispersible greenish yellow pigment powder is obtained which is particularly pure in the pure shade and which has high hiding power.

#### EXAMPLE 11

25 250 parts of the ground material obtained according to Example 1(a) is introduced into 500 parts of acetone and the mixture is stirred for eighty hours at ambient temperature. 30 2500 parts of water is then added and the whole is filtered. The filter residue is washed well and dried at 80°C in a through-circulation cabinet.

A very pure, deep-shade, yellow pigment is obtained which has high transparency and similar properties to the yellow pigment obtained according to Example 3.

As will be appreciated from the foregoing specific Examples the invention provides a process enabling the production of deep-shade greenish yellow pigments of outstanding fastness to light, migration and weather and resistance to high temperature.

#### WHAT WE CLAIM IS:—

45 1. A process for the conversion into pigmentary form of a chloro- and/or bromo-substituted phthalimidoquinophthalone crude pigment which process comprises grinding the crude pigment optionally in the presence of a grinding aid until the mean size of the primary particles is less than 0.5 micron and contacting the so ground crude pigment with an organic liquid.  
50 2. A process as claimed in claim 1 wherein the crude pigment is ground in the absence of a grinding aid.  
55 3. A process as claimed in claim 1 or 2 wherein the crude pigment is ground until the mean size of the primary particles is not more than 0.1 micron.  
60 4. A process as claimed in any of claims 1 to 3 wherein the organic liquid used is a

primary, secondary or tertiary aliphatic alcohol, araliphatic alcohol or cycloaliphatic alcohol, or an aliphatic ketone, cycloaliphatic

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ketone, aliphatic-aromatic ketone, lower aliphatic carboxylic acid, lower aliphatic carbamate, aliphatic or cyclic saturated ether, cyclic hydrocarbon, aromatic chlorohydrocarbon or nitrohydrocarbon or a mixture of two or more thereof.

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5. A process as claimed in any preceding claim wherein the contact of the ground crude pigment with the organic liquid is maintained until the pigment has optimum colour strength.

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6. A process as claimed in any preceding claim wherein the contact of the ground crude pigment with the organic liquid is effected using the organic liquid in an amount of from 0.5 to 3 parts by weight per part by weight of ground crude pigment.

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7. A process as claimed in any preceding claim wherein the crude pigment is dry ground and the dry ground crude pigment is contacted with the organic liquid.

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8. A process as claimed in any one of claims 1 to 6 wherein the crude pigment is subjected to grinding in the presence of the organic liquid.

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9. A process as claimed in any preceding claim wherein contact of the ground crude pigment with the organic liquid is effected at a temperature of from room temperature to 80°C.

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10. A process as claimed in any one of claims 1 to 7 wherein contact of the crude pigment ground with the organic liquid is effected at a temperature of from 130° to 200°C.

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11. A process as claimed in any preceding claim wherein grinding of the crude pigment is carried out in a ball mill or a vibratory mill.

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12. A process for converting into pigmentary form a chloro- and/or bromo-substituted phthalimidoquinophthalone crude pigment which process comprises dry grinding the crude pigment, optionally in the presence of a grinding aid, in a ball mill or vibratory mill at a temperature of from room temperature to 200°C, to produce a ground material comprising particle agglomerates composed of primary particles having a mean size of not more than 0.1 micron, forming a suspension of the ground material in an organic liquid and removing the organic liquid from the suspension after the ground material has remained in contact with the organic liquid for a desired length of time determined as that required to produce a pigmentary form product having a desired level of tintorial strength.

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13. A process as claimed in claim 1 and carried out substantially as described in any one of the foregoing Examples.

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14. Chloro- and/or bromo-substituted

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phthalimidoquinophthalone in pigmentary form, whenever obtained by a process as claimed in any preceding claim.

5 15. A phthalimidoquinophthalone containing chlorine and/or bromine and in a pigmentary form as identified in any of the foregoing Examples.

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